

Photocapacitive Behavior of Nanostructured Semiconductor/Electrolyte Interfaces

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In this paper, we focus on the photocapacitive behavior of two semiconductors, n-TiO₂ and p-CuSCN, in contact with aqueous media. In the former case, Degussa P-25 TiO₂ films were coated on polycrystalline Au substrates. In the latter case, p-CuSCN was anodically grown^{1, 2} in an alumina template matrix. We show that in both these instances, the photoinduced charge at the interface (from band-gap illumination of the semiconductor) results in interesting data trends, that can be potentially put to practical use in applications such as photon flux meters and the like.

Figure 1 contains representative data for the TiO₂ system.³ The linear relationship observed between the light-induced potential shift (ΔE_{ph}) and the incident photon flux underlines the photocapacitive property of the TiO₂-based aqueous interface. Computer simulation results will be presented to support the veracity of a simple photocharging interface model for this system. The depolarizing influence of several metal ions on the photocapacitive behavior will also be described, as are the effects of co-additives such as formate ions.

The second system comprises of a thin alumina template in which p-CuSCN nanodots are anodically grown (Figure 2).⁴ It is shown how the photoresponse may be amplified (from a low level typical of the of the signal emanating from a $\sim 10^{-11}$ cm² region corresponding to a semiconductor nanodot) by using a larger number of electrically inter-connected Au nanowires to support the overlying semiconductor nanodots. Interestingly these p-CuSCN nanodots showed anomalous photocurrent (or photopotential) vs. time transients that were distinctly different from the corresponding *macrosized* film counterpart.

Figure 3 contains representative computer simulations of this rather unusual transient behavior. These numerical simulations used a simple parallel equivalent circuit consisting of a semiconductor and a photocapacitor. We show that Cu-clusters formed in situ on the irradiated p-CuSCN surface serve as charge storage centers with the entire interface then behaving as a photocapacitor. Such behavior is strikingly reminiscent of the behavior of diode-array photon detectors. While such (Si-based) arrays are currently manufactured by lithographic procedures, our data suggest that less expensive alternative preparation routes (such as template-directed electrosynthesis) may be deployed for the development of a new generation of diode array detectors.

References

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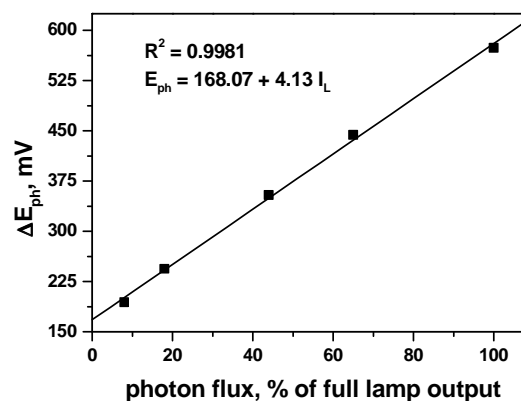


Fig. 1. Linear dependence of the photopotential on the incident photon flux for the TiO₂/electrolyte interface.

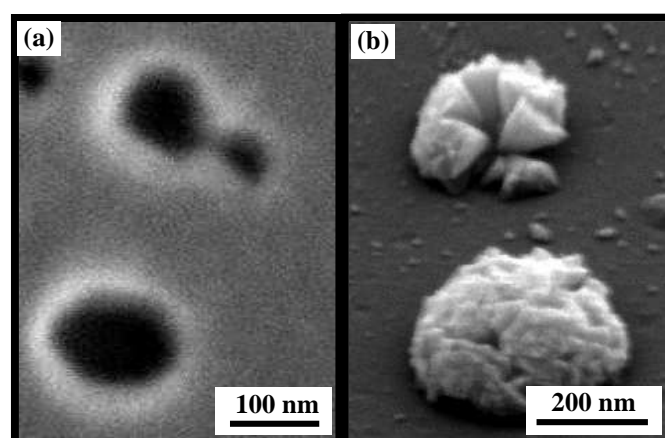


Fig. 2. Scanning electron micrographs of the alumina template before (a) and after (b) electrosynthesis of p-CuSCN.

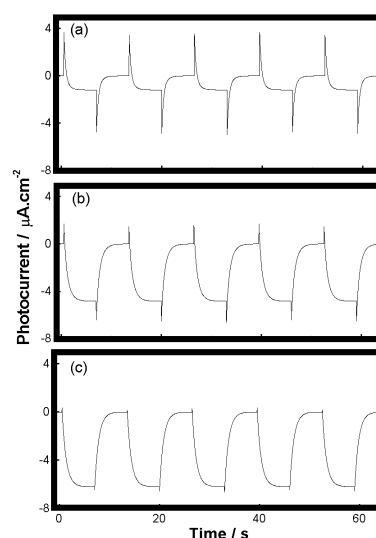


Fig. 3. Numerical simulations of the photocurrent transients at three different potentials for p-CuSCN nanodots.